952. *Nitratopentacarbonylmanganese*(I).*

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The preparation of nitratopentacarbonylmanganese(I), the first nitrato-metal carbonyl, is reported. The infrared and ultraviolet spectra, thermal stability, conductivity in solution, solubility properties, and some reactions of the compound are discussed. Where appropriate, comparison is made with the pentacarbonylmanganese(I) halides.

NUMEROUS derivatives of the metal carbonyls are known in which one or more of the carbonyl groups are replaced by neutral ligands such as amines and alkyl- or aryl-substituted phosphines and arsines.[1] Less abundant, but equally well characterised, are derivatives in which negative ligands such as iodide, bromide, and chloride replace carbon monoxide groups in the carbonyls with resultant oxidation of the central metal.[2] These halide ions have empty *d*-orbitals which can participate in the π-bonding to the metal and thus stabilise its low-valency state.

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* For a preliminary note, see *Proc. Chem. Soc.*, 1961, 202.

[1] See, *e.g.*, the review by Hieber, *Angew. Chem.*, 1952, **64**, 465.

[2] See Anderson, *Quart. Rev.*, 1947, **1**, 331.

In view of the respective properties of carbon monoxide and the nitrate group, the nitrato-carbonyls might be expected to display very low stability. The nitrate group is a good oxidising agent and is not normally regarded as capable of stabilising low-valency states in transition metals, particularly if the latter are combined with good reducing ligands, such as carbon monoxide. Again, if the nitrate group co-ordinates through a single oxygen atom, the latter possesses no empty orbitals which could be used for π-bonding with the metal. It is therefore not surprising that no nitrato-carbonyl has previously been prepared.

In order to investigate the possibility of preparing a nitrato-carbonyl, manganese compounds were chosen for two main reasons. First, pentacarbonylmanganese halides are stable, crystalline compounds which are almost certainly octahedral. The maximum stability of the metal carbonyl halides is attained with manganese compounds, and there was reason to believe that a manganese carbonyl nitrate would be also the most stable representative of this class of compound. Secondly, dimanganese decacarbonyl is soluble in a wide range of solvents, which enabled solvent effects to be explored.

Attempts were first made to bring about direct substitution of the nitrate group for chloride and bromide in pentacarbonylmanganese halides, by using silver and lead nitrate in ethyl alcohol. With silver nitrate, solutions decomposed rapidly, and lead nitrate gave inseparable mixtures of products. The scale of the reactions with lead nitrate was also limited by the low solubility of this salt, and this approach was found to be impracticable. Reaction of dimanganese decacarbonyl and dinitrogen tetroxide was then examined.

The conditions chosen were based on observations made in a preliminary survey of the reactions between metal carbonyls and liquid dinitrogen tetroxide, which will be summarised briefly. The rate of reaction depends greatly on the physical state of the metal carbonyl. Liquid carbonyls (nickel tetracarbonyl and iron pentacarbonyl) react violently: solid carbonyls react much more slowly, and reaction rate is a function of surface area. All reactions are strongly dependent on temperature; dimanganese decacarbonyl and dicobalt octacarbonyl react quite readily with dinitrogen tetroxide at room temperature but reaction stops almost completely at 0°. The reaction with nickel tetracarbonyl, which proceeds with explosive violence at 0°, can be moderated somewhat at lower temperature.[3] Finally, solid cyclopentadienyl-metal carbonyls react much more readily than the solid simple carbonyls; cyclopentadienyltricarbonylmanganese, the most inert and stable of these compounds, ignites readily when added to liquid dinitrogen tetroxide.[4] The ultimate products of these reactions are anhydrous metal nitrates, oxide nitrates, or their dinitrogen tetroxide addition compounds.

The rate of reaction of dimanganese decacarbonyl was sufficiently slow for isolation of intermediate products to appear possible. The reaction was readily controlled in an excess of a solvent, but the nature of the reaction was found to depend on the particular solvent used. In ethyl acetate, reaction was very slow. In nitromethane, reaction was instantaneous, but the product separating from solution contained no carbonyl groups. In light petroleum, a yellow precipitate was formed which showed strong carbonyl absorption bands in the infrared region, and it is from this product that nitratopentacarbonylmanganese(I) has been isolated.

EXPERIMENTAL

Dimanganese decacarbonyl was purified by sublimation at 50°/0·1 mm. Dinitrogen tetroxide was prepared as already described.[5] Light petroleum (b. p. 40—60°) was dried over phosphoric oxide and distilled. Chloroform was washed with water to remove traces of alcohol, dried ($CaCl_2$), and freshly distilled from phosphoric oxide.

Preparation of Nitratopentacarbonylmanganese(I).—Dimanganese decacarbonyl (4 g., 0·01

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[3] Addison and Johnson, unpublished results.

[4] Addison and Wojcicki, unpublished results.

[5] Addison and Thompson, *J.*, 1949, S218.

mole) was dissolved in light petroleum (250 ml.), and the solution cooled to 0°. Dinitrogen tetroxide (12 g., 0·13 mole) in light petroleum (5 ml.) at 0° was then poured into the carbonyl solution in a closed system vented to air by a phosphoric oxide guard tube. On mixing, the yellow solution of the carbonyl became deep orange and after 30 sec. became cloudy and a flocculent yellow precipitate separated. The temperature was maintained at 0° for about 40 hr., after which precipitation appeared to be virtually complete. There was no apparent change in the precipitate during the course of its formation. After 40 hr. the solvent was decanted, the residue washed with light petroleum (3 × 25 ml.) to remove traces of unchanged dimanganese decacarbonyl, and dried under reduced pressure. This residue was shown (by infrared spectrum, solubility, and elementary analyses) to be a mixture of several products. To allow the less stable impurities to decompose, the powder was allowed to remain in a dry atmosphere for 3 days, during which its colour darkened to light brown. It was then extracted with successive 10 ml. portions of pure chloroform at room temperature. Light petroleum (about 20 ml.) was added to each extract, and the solutions were cooled in acetone–solid carbon dioxide. A series of precipitates was thus obtained which were examined for purity by analyses and infrared spectra. Precipitates from early extracts were mixtures of several products; later ones consisted of nitrato- and nitro-pentacarbonylmanganese(I); and finally pure nitratocarbonyl was obtained in the last fractions. Further samples of $Mn(CO)_5NO_3$ were isolated by fractional crystallisation of the middle portions. The pure product was obtained as a bright yellow powder.

Analyses.—For manganese content the compound was dissolved in nitric acid; the solution was boiled to oxidise the metal to manganese(II), treated with sodium bismuthate to convert manganese(II) into manganese(VII), and titrated with standard ferrous solution. Nitrogen was determined by the Kjeldahl method. Carbon was determined by combustion to carbon dioxide, with vanadium(V) oxide. In view of low values often obtained with metal carbonyl derivatives, carbon analyses were confirmed by first oxidising the material vigorously in a closed system with a mixture of chromic oxide, phosphoric acid, fuming sulphuric acid, and potassium iodate, and then determining carbon dioxide by absorption[6] (Found: Mn, 21·5; N, 5·55; C, 23·3. C_5MnNO_8 requires Mn, 21·4; N, 5·5; C, 23·4%).

Magnetic Susceptibility.—Measurements were made at room temperature by the Gouy method, with finely powdered samples.

Infrared Spectra.—Routine infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer. The spectrum of the pure product was obtained by using a Unicam S.P. 100 spectrophotometer with sodium chloride windows, and Nujol and hexachlorobutadiene as mulling agents.

Molecular Weight.—This was determined cryoscopically in nitrobenzene, which had been purified by distillation and fractional crystallisations. For a $3·2 \times 10^{-2}$M-solution of the compound, a molecular weight of 254 was obtained [Calc. for $Mn(CO)_5NO_3$: *M*, 257].

Electrical Conductivities.—Conductivity of solutions was measured by using the circuit[7] and conductivity cell[8] described elsewhere. For the conductivity measurements, pentacarbonylmanganese halides were prepared by methods described in the literature.[9,10] Nitromethane was dried over calcium chloride and phosphoric oxide, refluxed under argon, and distilled from phosphoric oxide. Deionised water and spectroscopic-grade ethyl alcohol were used.

Ultraviolet Spectra.—These were determined in chloroform by means of a Unicam S.P. 500 spectrophotometer and 0·5 cm. matched fused silica cells.

Reactions of Bromopentacarbonylmanganese(I).—(a) *With silver nitrate.* This reaction was carried out on a test-tube scale. A saturated solution of silver nitrate in ethyl alcohol was added to an equimolar solution of $Mn(CO)_5Br$ in the same solvent. The mixture darkened almost instantaneously and a black precipitate was formed. No nitro- or nitrato-carbonyls were detected in solution.

(b) *With lead nitrate.* Various conditions were tried with ethyl alcohol as solvent, but results were not reproducible. Chromatographic separation, on alumina, was not successful

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[6] Dunstan, personal communication.

[7] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.

[8] Groeneveld and Zuur, *Rec. Trav. chim.*, 1953, **72**, 617.

[9] Brimm, Lynch, and Sesny, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.

[10] Abel and Wilkinson, *J.*, 1959, 1501.

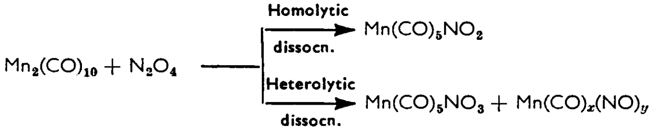
because of low stability of the products. Infrared spectra indicated a mixture of several products but the yields were too low to attempt separation.

Other Reactions of Dimanganese Decacarbonyl with Dinitrogen Tetroxide.—(a) *In ethyl acetate.* Dimanganese decacarbonyl (0·5 g.) in ethyl acetate (40 ml.) was mixed with dinitrogen tetroxide (5 g.) in ethyl acetate (15 ml.) at room temperature. After 20 hr. the solvent and the tetroxide were removed under reduced pressure. The yellow residue was washed with light petroleum and then recrystallised from chloroform–light petroleum. Infrared spectrum showed the presence of carbonyl, nitro-, and nitrato-groups. These products were not separated, since this technique offered no advantage over the use of light petroleum.

(b) *In nitromethane.* Dinitrogen tetroxide (4 g.) in nitromethane (5 ml.) was added to dimanganese decacarbonyl (1 g.) in nitromethane (30 ml.) at room temperature. The solution became green, and vigorous evolution of gas occurred. Slow separation of a white solid began after about 2 hr.; the infrared spectrum of this solid showed no carbonyl bands.

RESULTS AND DISCUSSION

Several products are formed in the reaction of dimanganese decacarbonyl with dinitrogen tetroxide in light petroleum. A surprising feature is the predominance of the nitrato-carbonyl, $Mn(CO)_5NO_3$, since the ionisation $N_2O_4 \longrightarrow NO^+ + NO_3^-$ is at its minimum in non-donor solvents.[11] The formation of nitrato-carbonyl may well be due to preliminary association of dimanganese decacarbonyl with the tetroxide, possibly as an addition compound, in which the tetroxide then undergoes heterolytic rather than homolytic dissociation. The general reaction scheme is:



In view of the formation of a nitrate complex, the NO group must also be produced, either as a nitrosyl carbonyl or as nitric oxide in solution. No gas evolution was observed, and freezing the reaction mixture at frequent intervals gave no blue colour due to dinitrogen trioxide. However, the crude product gave infrared absorption bands at 1650 and 1560 cm.$^{-1}$; these are attributed [12] to a manganese nitrosyl carbonyl which is more soluble than the nitrato-carbonyl in chloroform, and is thus removed on fractional crystallisation.

There is also clear evidence for the formation of nitropentacarbonylmanganese(I). The co-ordinated NO_2 group absorbs in the infrared region at about 1430, 1315, and 825 cm.$^{-1}$.[13] Middle fractions obtained on recrystallisation of the crude product contained absorption bands at about 1410, 1315, and 825 cm.$^{-1}$. Furthermore, analyses on these fractions showed nitrogen and manganese contents intermediate between those calculated for $Mn(CO)_5NO_3$ and $Mn(CO_5)NO_2$. The crude product also showed an absorption band at 1080 cm.$^{-1}$, which may be assigned to the nitrito-group. Nitro- and nitrito-pentacarbonylmanganese(I) were also more soluble in chloroform than the nitratocarbonyl, and were removed by fractional crystallisation.

TABLE 1.

Frequency (cm.$^{-1}$) ...	2060s	2002s	1486s	1284s	1010s	805w
Assignment	CO stretch		NO_2 stretch asymmetric	NO_2 stretch symmetric	NO stretch	$-O{\cdot}NO_2$ out-of-plane vibration

Infrared Spectrum.—Principal absorption bands of the final fractions, which did not change on further crystallisation, are given in Table 1.

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[11] Addison and Sheldon, *J.*, 1958, 3142, and references therein.

[12] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

[13] Penland. Lane, and Quagliano, *J. Amer. Chem. Soc.*, 1956, **78**, 887.

Pentacarbonylmanganese halides show two carbonyl absorption bands,[10] consistent with their C_4v symmetry. Since the nitrate group in co-ordination compounds is almost certainly planar,[14] the C_4v symmetry is to be expected for $Mn(CO)_5NO_3$ also, and two carbonyl stretching frequencies are in fact observed. The nitrate absorption bands leave no doubt that the nitrate group is covalently bonded to manganese.[15] Ionic nitrates exhibit only one NO_2 stretching band, at 1390 cm.$^{-1}$, and this is not observed in the spectrum.

Magnetic Susceptibility.—Nitratopentacarbonylmanganese(I), like the pentacarbonyl halides, is diamagnetic. These pentacarbonyls are d^6-octahedral, or distorted octahedral, systems, and have low spin values for their magnetic moment because of high polarisability and strong π-bonding ability of the carbonyl groups.[16]

Thermal Stability.—In the solid state at room temperature the compound is stable for several weeks. Pentacarbonylmanganese halides differ considerably from the nitrate in their volatility and thermal stability at higher temperatures. The chloride, bromide, and iodide, can be sublimed in a vacuum, and at 120° give univalent dimeric compounds of the type $[Mn(CO_4)X]_2$,[10] which on further heating decompose to their respective manganese(II) halides. The +1 oxidation state of manganese is less stable in the carbonyl nitrate than in the carbonyl halides. Heating at 55°/0·01 mm. causes disproportionation, and gives sublimed $Mn_2(CO)_{10}$ and a residue containing $Mn(NO_3)_2$ and some oxides of manganese. No $Mn(CO)_5NO_3$ was obtained in the sublimate, even on further heating. This disproportionation may be represented as:

$$4\mathrm{Mn(CO)_5NO_3} \longrightarrow \mathrm{Mn_2(CO)_{10}} + 2\mathrm{Mn(NO_3)_2} + 10\mathrm{CO}$$

When the compound is heated, carbon monoxide is first evolved; then dimanganese decacarbonyl sublimes and eventually dinitrogen tetroxide is evolved by decomposition of the nitrate. The two factors probably responsible for a lower stability of the nitrate are an increased ionic character of the molecule and a weaker overall π-bonding. The nitrate group is a weak ligand when co-ordinated through only one oxygen; some ionic character in the $Mn{-}O{\cdot}NO_2$ bond will render the metal positive and hence decrease the flow of its electrons to the carbonyl groups, *via* π-bonding. The overall effect will be a weakening of the Mn–CO bonds, as compared with the pentacarbonyl halides.

Solution Properties.—Increased ionic character of the compound $Mn(CO)_5NO_3$, as compared with the carbonyl halides, becomes apparent from the study of its solution properties. Conductivity measurements on fresh solutions of the nitrato-carbonyl in several solvents, and on solutions of the carbonyl halides in nitromethane, are compared in Table 2. The following points are noteworthy: (1) Each of the compounds is essentially a non-electrolyte in all of these solvents. The molar conductivities for uni-univalent

TABLE 2.

Molar conductivities.

Solute	Solvent	Temp.	Molar concn. $(\times 10^4)$	Molar conductivity μ (ohm^{-1} cm.^{2})	Age of solutions (min.)
$Mn(CO)_5NO_3$	$MeNO_2$	25°	71	0·48	3
	$MeNO_2$	0	70	0·098	3
	$MeNO_2$	24	40	<0·1	3
	EtOH	24	16	4·1	3
	H_2O	0	2	10·1	5
$Mn(CO)_5Cl$	$MeNO_2$	24	86	0·023	3
$Mn(CO)_5Br$	$MeNO_2$	23	93	0·007	3
$Mn(CO)_5I$	$MeNO_2$	24	114	0·004	3

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[14] Maxwell and Mosley, *J. Chem. Phys.*, 1940, **8**, 738.
[15] Addison and Gatehouse, *J.*, 1960, 613.
[16] Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 515.

electrolytes in nitromethane and nitrobenzene are of the order of 90 [17] and 25 ohm^{-1} cm.^{2},[18] respectively. The nitrate is an extremely weak electrolyte even in water.[19] (2) Molar conductivities in nitromethane increase in the order $Mn(CO)_5I < Mn(CO)_5Br < Mn(CO)_5Cl < Mn(CO)_5NO_3$. This order is consistent with polarizabilities of the negative groups, leading to differences in the ionic character of the Mn–X bonds. It is also similar to the trend observed for molar conductivities of pentacarbonylrhenium halides in acetone.[10] (3) The conductivities of solutions of the pentacarbonylmanganese compounds increase with time. The changes observed are illustrated for the nitrate and chloride in Table 3. The change in conductivity of the nitromethane solutions of the nitrate is arrested at lower temperatures and is then less than the change observed with the chloride. Aqueous solutions of the nitrate change very rapidly; measurements could not be made within the first five minutes because of slow rate of solution, but extrapolation of the values in Table 3 indicates that the nitrate first dissolves in water as a non-electrolyte.

TABLE 3.

Variation in molar conductivity (ohm^{-1} cm.^{2}) with age of solution.

			Age of solution (min.)				
Solute	Solvent	Temp.	3	5	15	30	60
$Mn(CO)_5NO_3$	$MeNO_2$	24°	0·48	0·77	2·3	4·4	7·2
$Mn(CO)_5NO_3$	$MeNO_2$	0	0·098	0·10	0·15	0·21	0·35
$Mn(CO)_5NO_3$	H_2O	0	—	10·1	13·8	26·2	34·5
$Mn(CO)_5Cl$	$MeNO_2$	23	0·023	0·098	0·40	0·70	1·3

This phenomenon can be explained on the basis of solvent replacement:

$$Mn(CO)_5NO_3 + \text{Solvent} \rightleftharpoons Mn(CO)_5\text{Solvent}^+NO_3^-$$

The formation of ionic species accounts initially for the conductivity of these solutions. The cation is unstable and on storage evolution of carbon monoxide from solution can be observed. The resulting decomposition products will no doubt be electrolytes, which contribute further to the increase in conductivity.

The molar conductivity values in non-aqueous solvents given in Table 2 are so low as to imply a negligible dissociation so far as the molecular weight of the solvent in fresh solutions is concerned, and the cryoscopic study of the nitrato-carbonyl in nitrobenzene confirms that the compound is monomeric and essentially undissociated in this medium.

The more polar nature of the Mn–NO$_3$ bond than of the M–Cl bond in these complexes is reflected in the solubility properties of the nitrato-carbonyl. It is readily soluble in alcohol, acetone, ethyl acetate, nitrobenzene, nitromethane, and chloroform; sparingly soluble in water, ether, methyl cyanide, benzene, and carbon tetrachloride; and insoluble in aliphatic hydrocarbons and carbon disulphide. Its solubility in water, although not large, is unusual since there are very few non-salt-like metal carbonyls which dissolve in water. Nitratopentacarbonylmanganese(I) in solution is much less stable than the carbonyl halides. Nevertheless, treatment of fresh aqueous solutions of the nitrato-complex does not lead to immediate oxidation of manganese(I) to manganese(II), and manganese(II) hydroxide is formed only slowly on heating.

Ultraviolet Absorption Spectra.—These were recorded for chloroform solutions in the region 280—420 mμ, and are summarised in Table 4. Dimanganese decacarbonyl, which absorbs much more strongly than the pentacarbonyl compounds, is given for comparison. Its ε value is much higher than that reported for dicobalt octacarbonyl, for which $\lambda_{max.} = 352$ mμ and $\varepsilon = 315 \pm 100$.[20] Iron pentacarbonyl [21] and nickel tetracarbonyl,[22] on the

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[17] Harris and Nyholm, *J.*, 1956, 4375.
[18] Parish, Thesis, University of London, 1958.
[19] Nyholm, *J.*, 1950, 2071.
[20] Cable, Nyholm, and Sheline, *J. Amer. Chem. Soc.*, 1954, **76**, 3373.
[21] Sheline, *J. Amer. Chem. Soc.*, 1951, **73**, 1615.
[22] Thompson and Garratt, *J.*, 1934, 524.

other hand, show no absorption peaks in this region. It is significant that $\lambda_{max.}$ and ε values for the pentacarbonylmanganese(I) compounds fall into the order found for molar conductivities.

TABLE 4.

Ultraviolet absorption spectra.

	Concn. (M)	ε	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)
$Mn_2(CO)_{10}$	0·0001	20,000	344	299
$Mn(CO)_5NO_3$	0·001	1,200	375	331
$Mn(CO)_5Cl$	0·002	620	377	339
$Mn(CO)_5Br$	0·002	420	386·5	346·5
$Mn(CO)_5I$	0·001	390	404	373

Chemical Reactions.—Nitratopentacarbonylmanganese(I) with an excess of liquid dinitrogen tetroxide gives the addition compound $Mn(NO_3)_2,N_2O_4$. Since the same product is obtained from the reaction of dimanganese decacarbonyl with an excess of the tetroxide, the nitrato-carbonyl is probably an intermediate in the latter reaction.

Preliminary studies have been made on the reaction of $Mn(CO)_5NO_3$ with pyridine. The product has been shown by infrared spectroscopy to contain pyridine, nitrate, and carbonyl groups, and may be analogous to the products obtained by Abel and Wilkinson [10] from the pentacarbonyl halides.

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